①

MOLECULAR MOTION AND ENERGY MIGRATION IN POLYMERS

Professor David Phillips
The Royal Institution
London
W1X 4BS

Contract Number DAJA 37-82-C-0265

Third Periodic Report

July 1983 - December 1983

87   10   00   13

1. We have continued during this phase of the work to concentrate upon time-resolved anisotropy measurements in synthetic polymers, and have also initiated a study on the fluorescence of poly(diacetylenes). In addition, we have further examined excimer formation in compounds which model poly(vinyl naphthalene), and have been greatly concerned with testing the adequacy of kinetic models used by us earlier to describe fluorescence in such polymers. Results are discussed briefly below under appropriate headings. (Great ... ...)

A. Time-resolved fluorescence anisotropy in poly(vinyl) naphthalene labelled

We have continued the study of the segmental motion of poly (vinyl) naphthalene and poly(acenaphthalene) labelled poly (methyl methacrylate), and have now obtained rotational relaxation data as a function of temperature. A complete report on these studies will be presented in the next periodic report.

B. Poly(vinyl aromatic) polymers, excimer formation

The decay of monomer fluorescence in many poly(vinyl aromatic) polymers has been shown by us and other workers not to be described well by a simple kinetic scheme due to Birks (Scheme 1) and used to explain excimer formation in simple free aromatic molecules in solution. We were able to fit the decay characteristics of monomer fluorescence empirically to three exponential components, and sought to attach physical significance to the rate constants so derived in terms of Scheme 2, in which a distinction is made between monomers which can easily form excimers M_1* in Scheme 2 through electronic energy migration and/or segmental motion, and those which cannot, M_2*[1]. Such a distinction is not unreasonable, and might for example correspond to sequences of dyads in isotactic regions of the polymer (M_1) and syndiotactic regions (M_2). However, our approach has been criticised recently by two groups of workers. Frederickson and Frank[2] show from a theoretical viewpoint that energy migration should not be modelled by a rate-constant, but by a time-dependent parameter, and show that the decay of monomer fluorescence should be modelled by a function of the form

$$i(t) = A \exp - (Bt + Ct^{\frac{1}{2}}) \qquad \dots\dots\dots\dots(1)$$

These authors stated that such a function could be approximated by a three exponential function, and thus to attach physical significance to parameters so derived was unwise. Itagaki et.al. adopted a different approach,[3] which was that electronic energy migration is very rapid, but segmental motion could not be modelled by a rate-constant, requiring again a function of exactly the same form as eq.(1). They took data from our work and showed them to be compatible with eq.(i). However, they did not apply the stringent tests of acceptability which as a matter of routine we apply, and

we have thus investigated our systems further. In no case could
expression (1) fit adequately our data[4]. Thus for example Figures
1, 2, 3 and 4 show respectively decay data on a random copolymer
of poly(styrene) with methyl methacrylate fitted to (a) expression
1 Fig. 1 (b) a two exponential decay function (Fig. 2) (c) and a
triple component function. It is clear that any model must be more
complex than expression (1), and we are currently investigating under
what circumstances a t^2 term could be uniquely identified in these
complex systems.

C. Model compound studies

Meso and racemic isomers of 2,4-diaryl pentanes provide good
models for isotactic and syndiotactic triads in vinyl(aromatic)
polymers. We have begun a study of such classes of compound,
beginning with the corresponding diaryl propanes, in this case
$\alpha\alpha$, $\alpha\beta$, and $\beta\beta$ diaryl naphthalenes. Results show the following
important features.

(i)   Steric constraints imposed by an ethane type linkage
between two naphthyl chromophores is sufficient to prevent
any excited state interactions. The quenching efficiency
of solvents on excited chromophores is restricted by the size
of the molecule to which the chromophore is tagged.

(ii)   The kinetics which govern intramolecular excimer
formation in $\alpha\alpha$-dinaphthylpropane can be described by the
simple Birk's kinetic Scheme (1). Evidence exists for a short
lived component, which may be caused by a small amount of a
less stable ground state conformation, and therefore use of
a more complex fitting function such as three exponentials
or a t^2 term may prove beneficial.

In view of the simple kinetics, use of this compound
as a probe for microviscosity measurements is valid, but not
for bulk viscosity measurements.

Relating the data to processes which occur in poly
(1-vinylnaphthalene) is unjustified, and in any case this
compound is not a valid model for this polymer. Further
investigations may indicate the existence of two stable
ground state conformers, in the event of such a result this
conclusion may be revised.

(iii)   In agreement with previous steady state measurements
on $\alpha\beta$-dinaphthylpropane, it appears that excited state complex
formation in this compound exists, and is attributed to a
partial overlap of the naphthyl chromophores. The stability
of this complex is low and consequently dissociation is rapid.
But surprisingly the rate of formation also appears to be rapid
indicating a low barrier of rotation between the stable ground
state conformer and the 'excimer' conformer.

(iv) It appear that during the preparation of ββ-dinaphthylpropane a species termed A* is produced which is structurally similar to BBDNP, but spectrally different[5]. The subsequent removal of this species from the sample studied, by presumably a photo-oxidative process and the spectral profiles are very similar to species observed in some vinyl naphthalene polymers. Thus in the work of Irie et.al.[6] and Nakahira et.al.[7] it is apparent that structures of the type assigned to A can appear in the spectra of naphthyl based polymers but not in a consistent fashion (i.e. dependent upon synthetic procedure). For example Irie et.al.[6] observe A* type emission from poly 1- and 2-vinylnaphthalenes whereas Nakahira et.al.[7] observe the emission in other naphthalene based polymers but <u>not</u> in poly(2-vinylnaphthalene). It is relevant to this discussion that the effects of tacticity proposed as one explanation for variations in the photo-physical behaviour of polymers such as poly (2-vinylnaphthalene) are based upon, in addition to studies of low molar mass analogues, observations of wavelength dependences of both excitation spectra and of excimer monomer ratio of emission spectra[8] which are very similar to those produced by the presence of the impurity A upon the spectra of BBDNP. Furthermore it has not been possible to reproduce the spectral dependence of polymer emission spectra with polymers and copolymers containing vinylnaphthalenes produced in our laboratories. The schemes proposed to account for anomalous emission in poly(vinyl) naphthalenes should in our view be regarded with scepticism.
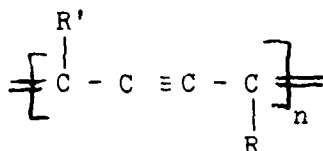

D.   <u>Poly(diacetylenes)</u>

The availability of macroscopic single crystals of poly-diacetylenes(PDAs) of a high degree of perfection has led to extensive studies of their properties over the last decade. Such perfect samples are obtained by the solid-state polymerisation of disubstituted diacetylene monomer crystals. The solid-state reaction of the 1 and 4 acetylenic carbons can be initiated by heat, pressure, ionising radiation (U.V., X- and γ-rays) and chemical radicals.
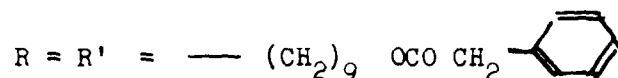
The intense optical absorption of PDAs is due to tne creation of excitons. The absence of fluorescence emission from PDA single crystals has, however, prevented any studies of exciton dynamics from being made. Fluorescence emission has been observed from monomers and the efficiency of the non-radiative decay channel for the perfect PDA chains is snown by the quencning of fluorescence when the monomer is converted into polymer. PDAs in which the extended chains are deformed in some way, i.e. partially polymerised crystals with high defect concentrations, mechanically deformed polymer, γ-ray polymerised crystals and solutions, do fluoresce. Very few detailed studies have been made of such fluorescence and the nature of the chain defects which allow radiative decay

to occur is a matter of conjecture. We have, therefore, initiated more precise studies of fluorescent emission from PDAs in order to obtain information about exciton motion and decay.

We have carried out some initial studies of the absorption, and fluorescence excitation and emission of a soluble PDA[9,10]. This is one of the class of soluble polymers obtained from the bis-esters of 10,12-docosadiyne-1, 22-diol which have the general structure:

$$\left[C - C \equiv C - C \right]_n$$

The particular polymer used was the bis-(phenyl acetate) ester, abbreviated 9PA, the chemical formula of which is given by:

$$R = R' = -(CH_2)_9 \ OCO \ CH_2 - \bigcirc$$

This polymer has a high molecular weight and is soluble in a range of common solvents.

Absorption, fluorescence excitation and emission spectra have been recorded at room and liquid nitrogen temperatures for different solvents. Spectral shifts, similar to those reported for other soluble polydiacetylenes, are observed on addition of a non-solvent or on cooling the solutions. The fluorescence quantum yield was measured from 2-methyltetrahydrofuran solution at room temperature. The yield was roughly one hundred times larger for this system at 77K and well-structured fluorescence spectra were observed for this low-temperature glass.

The spectroscopic studies of the 9PA/2-MTHF glass reveal that on quenching the yellow solution two distinct molecular conformations are produced. Annealing at room temperature for a short time and then re-freezing to 77K creates a third conformation apparently at the expense of one or both the initial conformations. This conformation cannot, however, be created directly from the yellow solution. These results are consistent with a model in which upon quenching random coil molecules are either frozen-in or partially recrystallise, full recrystallization to a chain-folded microcrystal occurring only after annealing at higher temperatures. Lifetime measurements are also compatible with the existence of different

conformations in low-temperature glasses which are retained for a considerable period at room temperature, the longer-lived species disappearing only when conversion to the random coil form is complete.

To explain the spectra of these conformations we invoke small local deformation in the form of twisting about the sp^2-sp^2 hybrid orbitals of the polymer backbone in the excited state. The excited state of trans-stilbene has a minimum for a $90°$ rotation about the double bond, smaller values have been observed in similar compounds. We suggest that a short-lived blue-shifted component of the total fluorescence occurs as a result of negligible change of the chain conformation, in the excited state. These, inter- or intra-chain interactions must lock this conformation in both ground and excited states. Conformations arising from a twisting of the double bond in the excited state are identified with the observed long-lived red-component of the total fluorescence. Further work is in hand to elucidate the chain conformations in 9PA glasses.

Literature cited

1. See for example D. Phillips, A.J. Roberts and I. Soutar.
    J.Polym.Sci (Polymer Phys. Ed.) 1980, 18, 2401.

2. G.H. Frederickson and C.W. Frank.
    Macromolecules. 1983, 16, 572.

3. H. Itagaki, K. Horie and I. Mita.
    Macromolecules. 1983, 16, 1395.

4. Reference (vi) in published work below.

5. Reference (v) in published work below.

6. M. Irie, T. Kamijo, M. Aikawa, T. Takemura, K. Hayashi and H. Baba.
    J.Phys.Chem., 1977, 81, 1571.

7. T. Nakahira, S. Ishizaka, S. Iwabuchi and K. Kojima.
    Macromolecules. 1982, 15, 1217.

8. F.C. De Schryver, K. Demeyer, M. van der Anweraer and E. Quanten.
    Ann. N.Y. Acad.Sci., 1981, 366, 93.

9. Reference (iii) in published work below.

10. Reference (iv) in published work below.

2.   The remainder of the contract will be carried out on the work
specified originally, plus further work upon the time-resolved fluorescence
of poly(diacetylenes) in solution phase and in glasses.

Papers published or presented during Grant Period

(i)   'Energy migration in poly(styrene)'
         D. Phillips, A.J. Roberts and I. Soutar.
         Macromolecules, 1983, 16, 1593.

(ii)   'Transient decay studies of photophysical processes in aromatic
         polymers. 7. Studies of the molecular weight dependence of
         intramolecular excimer formation in poly(styrene) and styrene-
         butadiene block copolymers.'
         D. Phillips, A.J. Roberts, G. Rumbles and I. Soutar.
         Macromolecules, 1983, 16, 1597.

(iii)   'Spectroscopic studies of poly(diacetylene) solutions and glasses'
         S.D.D.V. Rughooputh, D. Phillips, D. Bloor and D.J. Ando.
         Chem.Phys.Letters. (In press)

(iv)   'Chromism of a poly diacetylene with weakly interacting side groups'
         S.D.D.V. Rughooputh, D. Phillips and D. Bloor.
         Polymer Communications (Submitted)

(v)   'Anomalous emission in the fluorescence spectra of ββ-dinaphthyl
         propane: Investigation of the phenomenon of ground-state or second
         excimer intramolecular complexation in poly chromophoric species
         containing naphthalene'
         G.W. Arciero, C. Graham, D. Phillips, G. Rumbles and I. Soutar.
         Chem.Phys.Letters. (submitted)

(vi)   'On the modelling of fluorescence decay kinetics in poly(vinyl
         aromatic) polymers'
         G. Rumbles, D.Phillips and I. Soutar.
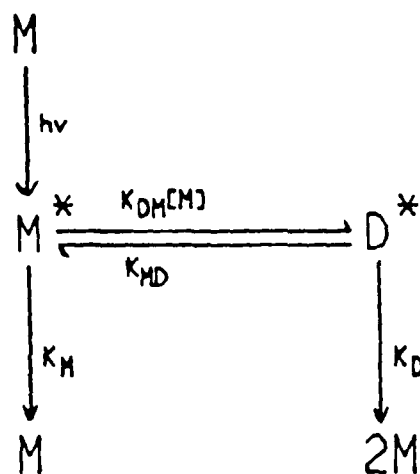   Macromolecules. (submitted)

3. The principal investigator lectured at the University of York, (Royal Society of Chemistry Lecture) on the subject of this research in December. At the end of this period of the contract, Mr. Garry Rumbles, one of the principal research workers involved, completed his Ph.D. requirements, and is now a post-doctoral fellow in the University of Arizona, Tucson, Arizona, USA. The work is being continued by Mr. R.C. Drake (anisotropy), Dr. Jean-Luc Gardette (on leave from CNRS Laboratoire de Photochimie, University of Clermont-Ferrand, France), (vinyl aromatic polymers), and Mr. S.D.D.V. Rughooputh (poly diacetylenes). Other than these changes in personnel, there has been no significant changes in the direction of the work.

Annex

5(a). The balance of unused funds remaining on the contract at the end of December 1983 is US $32,166
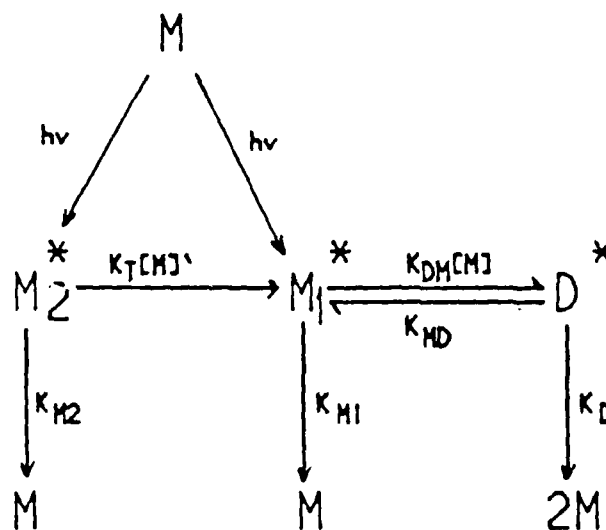
(b). Funds were expended upon partial salary for Professor R. Christensen and Mr. G. Rumbles, computational facilities, materials, refrigerants, and optical components including contribution to replacement ion-laser plasma tube.
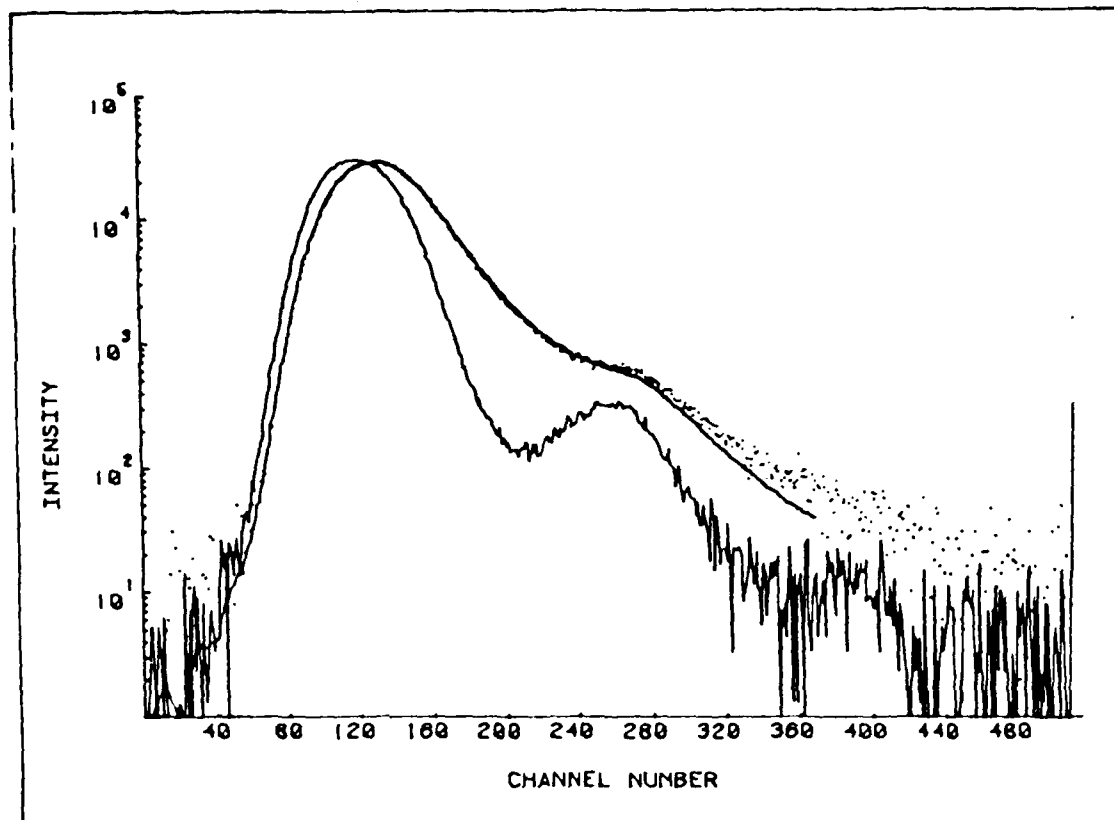
SCHEME I

$$M$$

$$\downarrow h\nu$$

$$M^* \underset{K_{MD}}{\overset{K_{DM}[M]}{\rightleftharpoons}} D^*$$

$$\downarrow K_M \qquad\qquad \downarrow K_D$$

$$M \qquad\qquad 2M$$

Kinetic scheme for excimer formation (BIRKS'scheme)

SCHEME II

$$M$$

$$h\nu \swarrow \qquad \searrow h\nu$$

$$M_2^* \xrightarrow{K_T[M]'} M_1^* \underset{K_{MD}}{\overset{K_{DM}[M]}{\rightleftharpoons}} D^*$$

$$\downarrow K_{M2} \qquad\qquad \downarrow K_{M1} \qquad\qquad \downarrow K_D$$
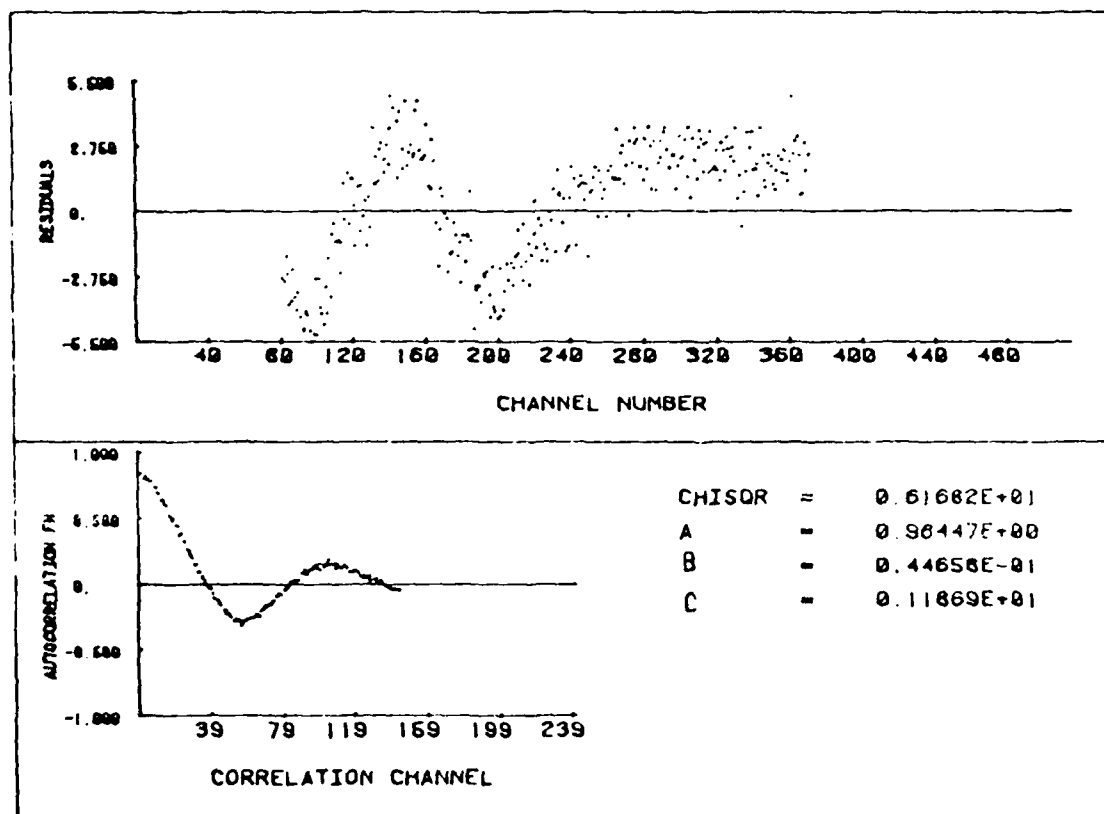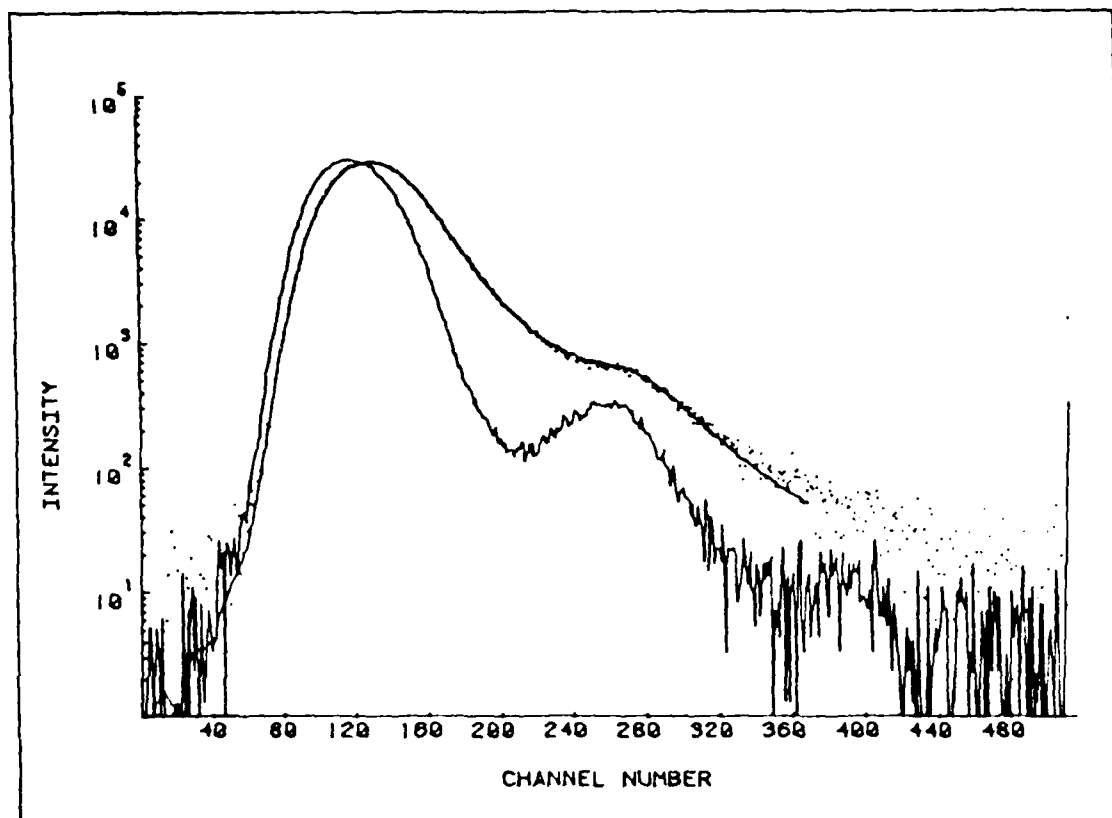
$$M \qquad\qquad M \qquad\qquad 2M$$

Kinetic scheme for intramolecular excimer formation in
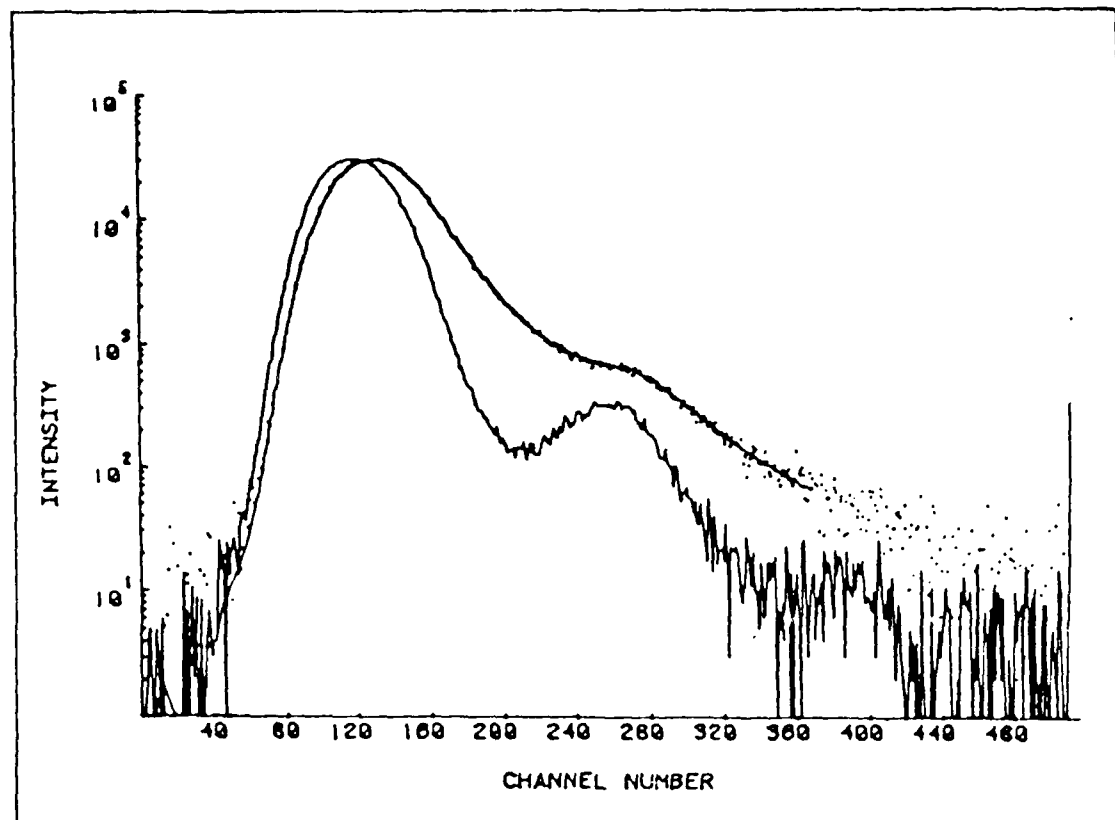styrene/methylmethacrylate copolymers.

Fluorescence decay of random copolymer sample 8 at 270nm
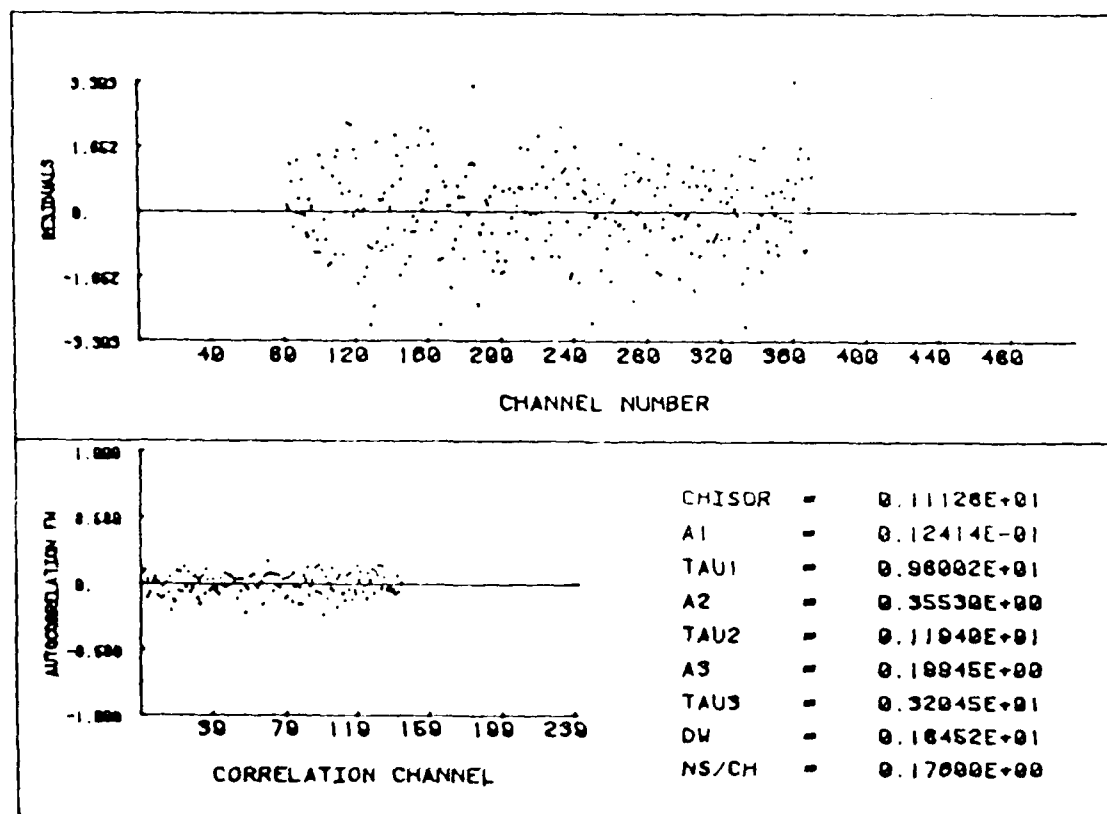
fitted to the function: $A.exp-(Bt+Ct^{1/2})$

CHISQR	=	0.61682E+01
A	=	0.96447E+00
B	=	0.44658E-01
C	=	0.11869E+01

Fluorescence decay of random copolymer sample 8 fitted to a
dual exponential function. (em. = 270nm)

CHISQR	=	0.15281E+01
A1	=	0.42838E+00
TAU1	=	0.22618E+01
A2	=	0.28474E-01
TAU2	=	0.77420E+01
DW	=	0.13326E+01
NS/CH	=	0.17800E+00
SHIFT	=	0.90000E+00

Fluorescence decay of random copolymer sample 8 at 270nm fitted
to a triple exponential decay function.

CHISQR	=	0.11126E+01
A1	=	0.12414E-01
TAU1	=	0.96002E+01
A2	=	0.35530E+00
TAU2	=	0.11940E+01
A3	=	0.18045E+00
TAU3	=	0.32045E+01
DW	=	0.16452E+01
NS/CH	=	0.17000E+00

END

Feb.

1988

DTIC